Development of Metal Chalcogenide Precursors for Use in Chemical Vapour Deposition (CVD) and Colloidal Nano Particle Synthesis

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Introduction

- Non-oxide group IV metal pnictogenides and chalcogenides semiconducting materials with medium and small band gaps (0.10 – 1.50 eV) have attracted considerable attention due to prospective applications in materials chemistry.
- These materials have been reported to have applications in sensors and laser materials, thin film polarizers, thermoelectric devices (**PbTe**), photo electrochemical (PEC) solar cells (**SnSe**), thin film photo-voltaics (**CZTS** and **SnS**), as well as cathode materials for lithium ion batteries.
- The poster presents our investigation into the design and synthesis of novel Tin chalcogenide systems.
- We have then investigated their viability as precursors for nano-particle formation or for Chemical Vapour Deposition (CVD) processes to produce desired tin chalcogenide thin films.

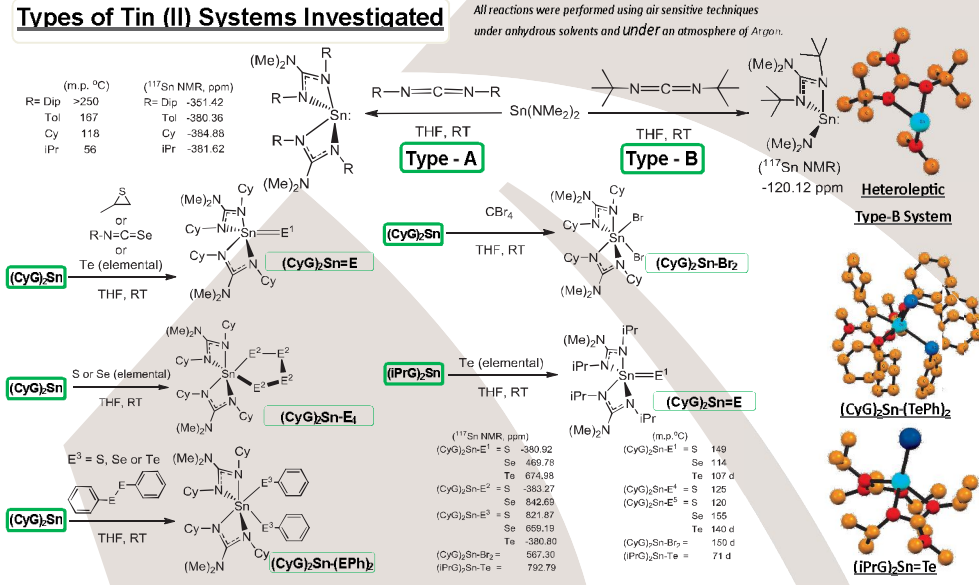
Metal Chalcogenide CVD Precursors

- Chemical Vapour Deposition (CVD) cab be used to produce nano-scale thin films. This technique requires volatile chemicals, known as precursors, in order to deposit thin films Desired features of a CVD precursor are:
  1) **Contain all the elements that are to be deposited (Single Source).**
  2) **Volatile and stable at required conditions (avoid polymeric compounds).**
  3) **Can degrade to deposit a thin film of the elements of choice.**
  4) **Cheap and facile to manufacture.**
- Metal amidinate systems have previously been shown to be viable as CVD precursors[1,2], it is of interest in this project to design similar Tin(II) Chalcogenolato Amidinates.

Design and Synthesis of New Tin Chalcogenide Precursors

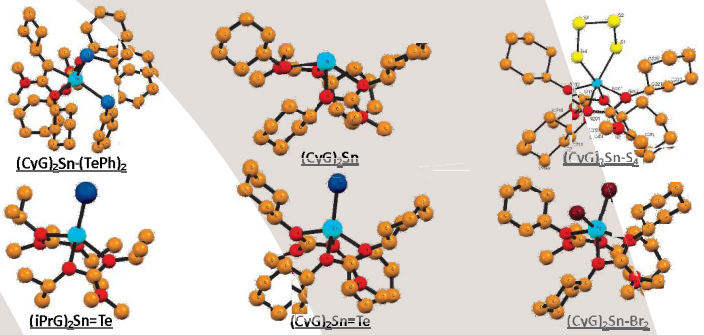
Types of Tin (II) Systems Investigated

All reactions were performed using air sensitive techniques under anhydrous solvents and under an atmosphere of Argon.

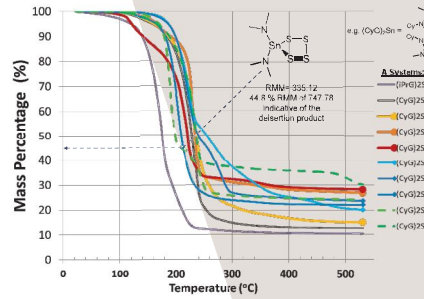


Synthesis of novel Tin Complexes:

- Tin Guanidinate systems **A** and **B** (**Left**) care synthised by reacting $Sn(NMe_2)_2$ with various carbodiimides.
- Bulky N,N'-Di-tert-butyl-carbodiimide results in mono-insertion and formation of the heteroleptic complex, type-**B** system, with a low melting point (<35°C).
- Less bulky carbodiimides (iPr, Cy, Dip and Tol) produce the di-inserted homoleptic complexes, type-**A** systems.
- Type-**A** systems were used to form mono, di, tetra-chalcogenide and halide complexes, via oxidative addition.

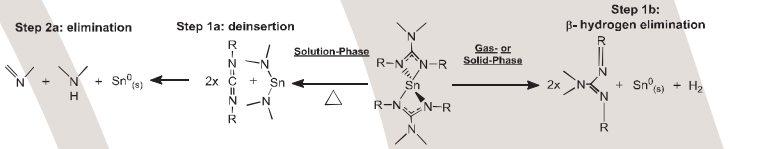


Thermal Decomposition Analysis of Type-A Systems



Thermal Gravimetric Analyses (TGA):

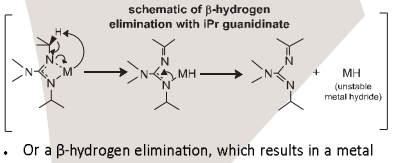
- The graph (**left**) is a series of TGA's for the type-**A** systems. Notice the Cy_2Sn-S_4 systems possibly under-goes a de-insertion decomposition step in the solid phase.
- Decomposition of the $(iPrG)_2Sn$: occurs at lower temperatures to the $(CyG)_2Sn$ (type-**A** systems)
- Instability maybe the result of a β-hydrogen elimination or the steric restrictions of the cyclohexyl groups.



Thermal Decomposition Pathways:

We predict that the Tin Systems, **A**, undergo two distinctive decomposition pathways in accordance to the guanidate ligands, as similarly investigated by S.T. Barry *et al* [4].

- Either a de-insertion, followed by reductive elimination/decomposition of the metal amide, in a 1e– reduction process.



- Or a β-hydrogen elimination, which results in a metal hydride formation and unsaturated ligand (above).
- The metal hydride can then decompose and release hydrogen gas.

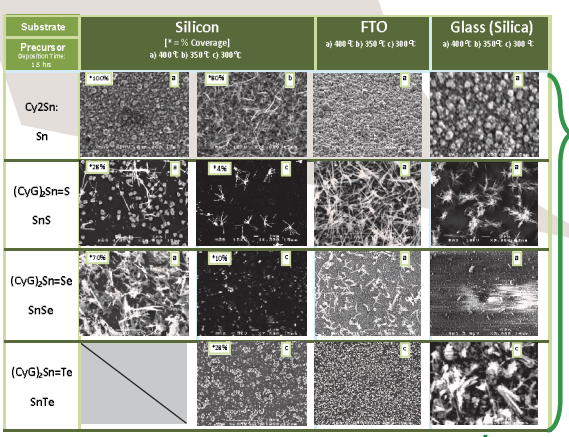
Using the Type-A Systems as AA-CVD Precursors

AA-CVD experiments were undertaken using the di-cyclohexyl functionalised systems (**A**) (Cy_2Sn: or Cy_2Sn=E, E = S, Se or Te).

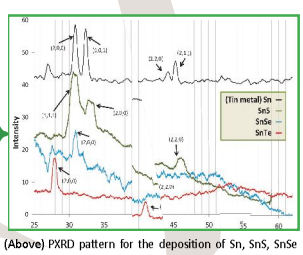
The **SEM images** presented on the right indicate a number of interesting features:

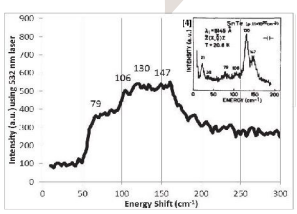
- Coverage Increases with Temperature
- Using a low concentration results in a non-continuous film
- Particles morphologies differ with temperature.

Powder X-Ray Diffraction (PXRD) and **Energy Dispersive X-ray Spectroscopy (EDS)** analysis on the different tin chalcogenide films, analysis show that we have deposited **Sn, SnS, SnSe** and **SnTe** thin films.



(Above) SEM images of the AA-CVD thin films of Sn, SnS, SnSe and SnTe produced from using the Cyclohexyl functionalised-C systems as precursors. All precursors were prepared as 0.033 M solutions in Toluene.





(Above) PXRD pattern for the deposition of Sn, SnS, SnSe and SnTe on a glass substrate. (Below) Raman Spectroscopy of SnTe deposition, using a 532 nm laser at 0.5 % intensity.

Raman Spectra

- Spectra show a broad range of peaks (50-200 nm) indicative of rock salt Raman inactive SnTe.
- When the SnTe film is heated with a laser, the Raman spectrum of elemental Tellurium is observed and persists.

Conclusion

- We have shown that the Guanidinate Tin Chalcogenide complexes can act as viable precursors for AA-CVD.
- We have shown deposition of Sn, SnS, SnSe and SnTe thin films.
- They exhibit a controlled decomposition step resulting the reduction of the tin metal centre.

In the future we aim to:

- Produce continuous 'SnE' films using the type-**A** systems.
- We will also investigate the new ligand systems with improved properties e.g. isopropyl functionalised guanidinate systems.
- Analyse the photo induce current of synthesised SnS, SnSe and SnTe nano-particle.

References:

[1] Lim, B. S., A. Rahtu, et al. (2003). Inorganic Chemistry 42(24): 7951-7958. [2] Becker, J. S. and R. G. Gordon (2003). Applied Physics Letters 82(14): 2239-2241
[3] Joe Thompson, MRes Research for First Project at the Centre for Sustainable Tech. (2013). [4] Barry, S. T., J. P. Coyle, et al. (2010). Inorganic Chemistry 49: 2844-2850
[4] Sugai, S., K. Murase and H. Kawamura. (1977). Solid State Communications 22: 127-129.

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